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Development and Fabrication of Carbon Nanotube (CNT) based Morphological and Electrical Characterization

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ABSTRACT

This paper presents the development and fabrication of carbon nanotube (CNT) based sensor devices through morphological and electrical characterization. The silicon oxide (SiO$_2$) as insulator is formed by dry oxidation process and Aurum (Au) layer is deposited using thermal evaporator. Then, the electrodes pattern is transferred by photolithography process. The single-walled carbon nanotubes (SWNTs) were mixed with isopropyl alcohol (IPA) for dispersion process. The suspended SWNT was aligned between the electrodes gap by using AC dielectrophoresis method. The composition of SWNT aligned was determined by the conductivity of SWNT aligned on devices was decreases as pH buffer solution increases. Capacitances value for pre-SWNT aligned is much higher than post-SWNT aligned.

Key words: Carbon Nanotubes, conductivity, capacitances.

Introduction

Carbon nanotube (CNT) has many excellent and unique properties that may encourage developing next generation of sensors since its discovery (Sinha, N., et al., 2006). CNT have exhibits some unique properties such as electrical, mechanical, and optical properties that can be rapidly integrated into many novel devices especially sensors devices (Liu, T.X., et al., 2004). These features was motivated to post CNT aligned sensor device have potential applications as a good semiconducting sensor devices build into different types of electronic, optoelectronic, and sensor system (Th. S., et al., 2010).

Single-walled carbon nanotubes (SWNTs) are class of material which is graphene sheets rolled up in certain directions designated by pairs of integers (Ajayan, P.M., 1999). In fact, SWNTs as 1D structure, atomically monolayered surface and extended π-bonding configuration have several unique properties like mentioned above (Ouyang, M., et al., 2002). For example, an individual SWNT with different chirality and diameter, it can be either semiconducting, metallic, or semimetallic, it able to be used as active conductivity in sensor devices due to their high current-carrying capacities (up to 10$^9$ Acm$^{-2}$) (Yao, Z., et al., 2000), and high thermal conductivities (up to 3500 Wm$^{-1}$K$^{-1}$) (Pop, E., et al., 2006).

For the SWNT alignment, there are two categories for SWNT attachment method which is direct growth and manual attachment of SWNT on electrode pads. Both the methods were found to be effective in attaching SWNT in the desired position. First of all, the growth technique of SWNT is often applied. However, it requires some patterning of very tiny catalysts and high temperature on the exact position (Jang, Y.-T., et al., 2004). However, it is extremely hard to get a uniform growth of SWNT for each catalyst.

Meanwhile, the manual attachment of SWNT is a low cost and effective method of SWNT attachment but it is not suitable for large scaled production due to long handling time, vacuum environment and expensive apparatus. Some of the manual attachment methods were found using chemical treatment (Yamamoto, K., et al., 1998), magnetic field (Long, D.P., et al., 2004), and electric field (Rao, S.G., et al., 2003) in the SWNT alignment process.

One of the useful for alignment techniques which is applying manual attachments method by using electric field is the AC dielectrophoresis. The dielectrophoresis (DEP) enable to control the assembly of individual SWNT on an electrode (Chung, J., et al., 2004). Meanwhile, two important results about fundamental study of the nanotube DEP and a large scale assembly technique of the nanotube by using DEP (Hennrich, F., et al., 2005). They reported that the advantages of DEP techniques is the position and number density of aligned CNTs can be controlled by adjusting the electric field.
Materials And Method

Materials:

Functionalized SWNTs-COOH (>97% carbon purity and <3% metal oxides impurities), IPA were purchased from sigma Aldrich, Malaysia. All materials were used as-received.

Preparation and fabrication of SWNT sensor devices:

First of all, fabrication processes begin from Si wafer cleaning with RCA1, RCA2, and Piranha solution. After cleaning, it was rinsed with DI water and then spun dry and loaded into modu-lab dry oxidation furnace with 1000°C for 60 minutes for dry oxidation process and silicon oxide (SiO2) layer was deposited.

After that it is undergo titanium/aurum (Ti/Au) layer deposition process by using thermal evaporator machine. The length of Ti is around 0.5cm while length of Au is around 1.0cm respectively was deposited onto SiO2 surface. It is brought for annealing process heating at 300°C for 10 mins and ramp down to 100°C in order to maintain the deposition layer.

After the layers were done, it was brought to the patterning process by using MIDAS MDA-400M Mask Aligner machine. In this photolithography process, few drops of photoresist (PR) were dropped onto the surface, the coating speed formula for ramp up is 1000rpm:10s, turning speed is 3000rpm:20s, and ramp down is 0rpm:10s, then heat it as soft bake process at 120°C for 3 mins. The wafer was taken to expose to the ultraviolet light for 10s. After that, the sample was brought to the development process by using pure photoresist developer solution. The pattern was developed in 40s. When patterned has appeared, hard bake process at 120°C for 3mins in order to maintain the photorersist layer patterned (Th. S., et al., 2011).

The next step is to etch the Au layer followed by Ti layer by using aqua regia solution. The aqua regia solution was prepared through a mixture of hydrochloric acids (HCl) and Nitric Acids (HNO3) in a ratio of 4:1. The aqua regia was then diluted in DI water in the ratio of 1:2 as the pure aqua regia is too strong and might destroy the patterned (Hashim, U., et al., 2012; Th. S., et al., 2011). Finally, the photoresist was stripped by using the acetone solution (Th. S., et al., 2011). The overall fabrication process was shown in Fig. 1.

Fig. 1: CNT Sensor Fabrication Process Flow

Morphological Characterization:

Once single strand of SWNT is aligned, the sample is brought to atomic force microscope (AFM), 3D profilometer, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) to perform morphological inspection. The AFM is used to observe the surface roughness condition of the sample to ensure the electrode is uniformly deposited onto the sample. The 3D profilometer is used to measure the thickness of the electrode deposited onto the sample. On the other hand, the SEM is used to inspect the condition of the SWNT alignment. Last but not least, the EDX is used to confirm that the alignment is indeed SWNT and not other materials.

Electrical Characterization:

The electrical characterization is performed to ensure the sensors are functional. The electrical characterization for this research is performed before and after alignment of SWNT between the electrode gaps with various pH buffer solutions. The frequency range of the dielectric analyzer which will be used to measure the conductance and capacitance is 1Hz – 100MHz with constant 0.5V of AC voltage. The results were obtained from the dielectric analyzer and plotted into graphs. From the plotted graph, a comparison of capacitance will be
made for before and after CNT alignment process. During the pH measurement process, solutions were dropped carefully using micro pipet onto the aligned SWNT between the electrode gaps. After each value of the pH solutions tested, the sample was cleaned with DI water and filter paper. The blower was used to dry the sample and make sure there is no dust on the sample. Sample was kept stationary with the probe needle location to avoid inaccurate results. Furthermore, sample was tested without any vibration or noisy environment to avoid bad results (Th. S., et al., 2011). The experimental setup was shown in Fig. 2.

Fig. 2: Electrical Characterization Experimental Setup

Results And Discussion

Atomic Force Microscopy Results:

Atomic Force Microscope (AFM) is a necessary part to investigate the surface roughness and grain size of Au electrode pad. The AFM image results were captured under 10000nm scan area. Fig. 3 shows typical AFM topography of the Au electrode surface after fabrication process. The roughness value, $S_d$, obtained from the corresponding AFM image is 2.15%. The roughness average of Au electrode gap is 1.430 nm whereas the grain size is 1.525 nm.$^2$.

Fig. 3: Atomic Force Microscopy (AFM) Topographic Image of Au Electrode Gap

A line profile of Au electrode gap obtained from the AFM topograph shown in Fig. 4. The inset shows the AFM image (1.0 µm x 1.0 µm, height scale 15nm) with a line indicating the location of line profile. The highest peak for the height is 11.94 nm with lateral distance with 3.47 nm.

Fig. 4: AFM Line Profile

3D Profilometer Surface Thickness Measurement:

After SiO$_2$ was deposited via dry oxidation process, Titanium (Ti) and Aurum (Au) layers were deposited by using thermal evaporator. The length of Ti used was 0.5cm whereas Au was 1.0cm. Due to the Au layer does
not very stick properly on SiO$_2$, a Ti layer was deposited in between of SiO$_2$ and Au in order to hold the Au layer so that the Au layer does not detach during the etching process. The results of Ti/Au thickness was measured by using 3D profilometer and shown in Fig. 5. The height of Ti/Au electrode of labeled P1 (white circled) spot is 146.6 nm and another spot labeled as P2 (white circled) is 142.5 nm.

![Fig. 5: Side View Electrode 3D Pattern](image)

From the Fig. 6, the Au electrode fabricated formed the gap with height around 106.2 nm for vertical measurement and 98.5 nm for horizontal measurement.

![Fig. 6: 3D Pattern of Au Electrode Gap](image)

The 3D profilometer surface analysis has shown 3D side view of electrode and the 3D pattern of Au electrode gap in Fig. 5 and Fig. 6, the results was shown non-uniform thickness. This problem could be caused by non-constant etching rate. During etching process with aqua regia solution, the photoresist was not strong enough to protect the pattern.

**Single Walled Carbon Nanotube (SWNT) Alignment Results:**

After the SWNT was successfully aligned, the sample was taken to Scanning Electron Microscope (SEM) for analysis. The SEM was shown in Fig. 7. The magnification results captured from Fig. 7 is x7000 magnification and well aligned SWNT between the Au electrode pads.

![Fig. 7: SWNT SEM Results](image)

**Single Walled Carbon Nanotubes (SWNTs) Energy-dispersive X-ray Spectroscopy (EDX) results:**

The SWNT aligned device was analyzed by using the energy-dispersive X-ray spectroscopy (EDX) of field emission scanning electron microscopy (FESEM). The EDX result has shown the composition of material as in Fig. 8. From Fig. 8, a spot was chosen from the aligned SWNT for EDX analysis. The carbon (C) element obtained major percentage up to 49.44%, oxygen (O) with 12.92% and silicon (Si) with 37.64% because the surface below the aligned SWNT is the silicon dioxide (SiO$_2$).
Fig. 8: EDX FESEM Results

**Electrical Characterization:**

To study the conductivity and capacitance of the device, electrical characterizations were carried out by using dielectric analyzer instrument. The following sections will present the results obtained before and after SWNT alignment and a comparison between the two. The mediums used in the test were pH buffer solution (pH) for pH3, pH5, and pH10, DI water and air.

**Device Conductance Results:**

For conductivity test of SWNT, there is no current flow before SWNT was aligned because of the device electrodes were separated by insulator. Therefore, this part test results were obtained only after SWNT was aligned between the electrode gaps (Th. S., U. Dhahi, Hashim, 2011). This conductivity test also applied AC electric field throughout the conductivity test.

The Fig. 9 shows the Conductivity (|Sig|) against Frequency (f) plot. It was shown that the conductivity was decreased from pH buffer solution pH3, pH5, to pH10. The conductivity for pH buffer solutions for pH3, pH5, and pH10 are 13.37µS/cm, 13.35µS/cm, and 13.02µS/cm respectively. On the other hand, the conductivity of DI Water buffer solution is slightly lower than the three pH buffer solutions with a conductivity of 12.98µS/cm.

**Device Capacitances Results:**

After that, a comparison of the capacitance value for before and after SWNT aligns devices was plotted into graph as in Fig. 10. From Fig. 10, the capacitance value for before SWNT alignment is much higher than after SWNT alignment. This is because before the SWNT alignment, the capacitor structure consist of conductor-insulator(SiO₂)-conductor whereas after the SWNT alignment, the capacitor structure consist of conductor-semiconductor(SWNT)-conductor. Another explanation for capacitance concept is the decreases of the effective electric field between the plates and will increase the capacitance of the parallel plate structure. The dielectric must be a good electric insulator in order to minimize any DC leakage current through a capacitor. Means that for before SWNT aligned, the sensor detection is in air condition as dielectric insulator, the air insulator will decrease the electric field giving high capacitance (Th. S., et al., 2012; Th. S., et al., 2012; Th. S., et al., 2012). In other words, the electric field is inversely proportional to capacitance. Therefore, the lower the electric field, the higher the capacitance (Nazwa Taib, et al., 2011).
In conclusion, we successfully aligned the SWNT on Aurum (Au) electrodes pad by using AC Dielectrophoresis method. When the pH increased, the conductance decreased. Whereas, as the pH values decreased as in acidic solution, the conductivity of electricity increased thus the capacitance decreased due to the electric field is inversely proportional to the capacitance. The SWNT aligned device has lower capacitance than the pre-aligned device. Our sensor device has highly potentially to immobilize and hybridize DNA onto the SWNT aligned device for Halal, protein or disease detection.

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